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(71) Applicant (for all designated States except US): **JOHNSON MATTHEY PUBLIC LIMITED COMPANY** [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **POLLINGTON, Stephen, David** [GB/GB]; 17 Chancer Close, Emmer Green, Reading RG4 8PA (GB). **POULSTON,**

Stephen [GB/GB]; 4 Hatherley Road, Reading RG1 5QA (GB). **TORBATI, Reza** [GB/GB]; 29 Merryman Drive, Crowthorne, Berks RG45 6TW (GB). **RAJARAM, Raj Rao** [MU/GB]; 34 Buckland Avenue, Slough SL3 7P11 (GB).

(74) Agent: **NUNN, Andrew, Dominic**; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).

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(54) Title: EXHAUST SYSTEM INCLUDING HYDROCARBON SCR CATALYST

(57) Abstract: An exhaust system for an internal combustion engine comprises a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst comprising a metal on a support, which support comprises alumina, titania, zirconia or, non-zcolite silica-alumina or a mixture or mixed oxide of any two or more thereof and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, wherein the exhaust system comprises means for coking the catalyst during normal engine operation.

EXHAUST SYSTEM INCLUDING HYDROCARBON SCR CATALYST

5 This invention relates to an exhaust system for an internal combustion engine, and in particular it relates to an exhaust system including a hydrocarbon selective catalytic reduction catalyst comprising a supported metal.

 In selective catalytic reduction (SCR) by hydrocarbons (HC), HC react with
10 NO_x, rather than with O₂, to form nitrogen, CO₂ and water according to equation (1):



15 The competitive, non-selective reaction with oxygen is given by Equation (2):



 Two preferred groups of HC-SCR catalysts to selectively promote the desired
20 reaction (1) for catalysing HC-SCR of NO_x (HC-SCR catalysts are also referred to as "lean NO_x catalysts" (LNC) or "DeNO_x catalysts"). These are platinum on alumina and copper-substituted zeolite such as Cu/ZSM-5.

 Pt-based catalysts tend to operate at relatively low temperature (peak activity
25 ~250°C) and have a relatively narrow temperature window for HC-SCR activity. Another problem is that the popular Pt/Al₂O₃ favours the formation of N₂O over N₂ at relatively low temperatures.

 Zeolite-based HC-SCR catalysts have a wider temperature window than Pt-based
30 HC-SCR catalysts and also operate at higher temperatures (peak activity ~400°C). However, a problem associated with zeolite-based HC-SCR catalysts such as Cu/ZSM-5 is that they can become deactivated in use through lean hydrothermal ageing. This is caused by sintering of the copper component and/or de-alumination of the zeolite.

One approach to address the problem of limited temperature window is to combine two or more HC-SCR catalysts (e.g. to combine both Cu/ZSM5 and Pt-based catalysts together) to extend the operating window of the catalysts (see e.g. K.C. Kharas et al. SAE 982603). Another approach is to include a HC trap component in the exhaust system upstream or on the HC-SCR catalyst that adsorbs HC when the exhaust gas is at a temperature below the light-off temperature of the catalyst, and desorbs the HC when the catalyst is at or above light-off temperature (see for example EP-A-0830201). However, neither approach addresses the problem of zeolite-based HC-SCR catalyst deactivation.

Research into alternative and improved HC-SCR catalysts continues to be published in the literature. In "Surface properties and reactivity of Cu/ γ -Al₂O₃ catalysts for NO reduction by C₃H₆ Influences of calcination temperatures and additives", T.-W. Kim *et al.*, App. Cat. A: Gen. 210 (2001), 35, the authors refer to prior reported studies which show that certain supported metal oxide catalysts, such as alumina supported copper and copper aluminate, have similar HC-SCR activities compared with Cu/ZSM-5. The Kim et al. paper describes investigations into how calcination temperatures affect the activity of the copper-based catalysts.

Others have investigated Cu/ZrO₂ (K.A. Bethke *et al.*, Catalysis Today 26 (1995), 169 and C. Montreuil *et al.* in US-A-5,155,077) and Cu-Zr mixed oxide systems (K.A. Bethke *et al.* Catalysis Letters 25 (1994), 37) for NO_x reduction with hydrocarbon. However, G.P. Ansell et al., (205th ACS National Meeting, Denver, 29th March-1 April 1993) report that the activity of Cu/ZrO₂-type materials is severely inhibited by the presence of water in the gas feed, a component often omitted in the reported tests involving these catalysts.

F. Figueras *et al.*, Catalysis Today 42 (1998), 117 have reported that Cu on sulfated zirconias leads to an increase in NO_x reduction activity for HC-SCR using decane as the hydrocarbon when compared with the un-sulfated support. Pasel *et al.*, Applied Catalysis B 25 (2000), 105 have studied a number of metal supported sulfated ZrO₂ systems including Cu using propane as the reductant.

US patent No. 6,202,407 describes a system in which HC is injected in a pulsed manner upstream of a HC-SCR catalyst e.g. Cu on Al₂O₃. The document explains that NO_x conversion in the system does not drop to zero when HC injection is stopped.

5 We have now devised an exhaust system comprising at least two specific HC-SCR catalysts, which system having a broader overall temperature window of NO_x reduction activity.

10 According to a first aspect, the invention provides an exhaust system for an internal combustion engine, which exhaust system including a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst comprising a metal on a support, which support comprises alumina, titania, zirconia or, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof, and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, wherein the exhaust
15 system comprises means for coking the catalyst during normal engine operation.

20 An advantage of the invention is that the temperature at which the first HC-SCR catalyst stores activated HC is also within the temperature range at which the second, Pt-based catalyst is effective for HC-SCR. The activation of the first catalyst at this temperature only results in a HC conversion of ~10% over the first catalyst. Hence up to 90% of the HC is available to the Pt-based catalyst for HC-SCR disposed with and/or downstream thereof. The activated first HC-SCR catalyst is available for HC-SCR at higher temperatures. Furthermore, the Pt-based catalyst can oxidise the CO produced by the preferred HC-SCR catalyst according to the invention as a by-product of generating
25 the activated hydrocarbon species.

30 By "coking" we mean contacting the catalyst with elevated quantities of hydrocarbon. We believe that this procedure leads to the formation of adsorbed activated hydrocarbon (or "coke") species on the catalyst surface.

By "elevated" herein, we mean that the quantities of hydrocarbon to which the catalyst is exposed are in excess of those quantities that would contact the catalyst during normal engine operation.

The coking means can be used to form the coke species on the catalyst surface by any convenient process e.g. by contacting a suitable HC liquid onto the catalyst surface, but preferably it is by introducing hydrocarbon into the exhaust gas. Preferred means for introducing hydrocarbon include at least one of: means for injecting the hydrocarbon into the exhaust gas; means for adjusting the ignition timing of at least one engine cylinder; and means for adjusting the engine air-to-fuel ratio.

Advantageously, the hydrocarbon is the fuel that powers the engine. The engine can be a stationary engine, but where it is used to propel a vehicle, this avoids the need to carry more than one source of hydrocarbon.

At its most fundamental, the means for coking the catalyst can expose the catalyst continuously to elevated amounts of hydrocarbon. However, we prefer that the exposure to hydrocarbon is intermittent and that the coking means further comprises means for controlling the coking process. Preferably, the control means includes a pre-programmed electronic control unit (ECU). For example, the ECU can carry "maps" to expose the catalyst to hydrocarbon responsive to driving conditions e.g. use of accelerator, engine revs and/or responsive to feedback from on-board diagnostics such as exhaust gas or catalyst temperature sensors, tailpipe NO_x sensors etc.

Preferably, the catalyst is exposed to hydrocarbon responsive to the catalyst temperature which can be measured directly or estimated according to exhaust gas temperature. For example, the control means can coke the catalyst at between catalyst temperatures at which hydrocarbon oxidation commences over the catalyst and peak NO_x conversion occurs. For catalysts for use in the present invention, this can occur in the temperature range 200-450°C, preferably 250°C to 350°C. Selective addition of HC at specific catalyst temperatures leads to improved utilisation of the added HC and so greater fuel economy.

A feature of the invention is that the HC-SCR catalyst are chosen to have improved resistance to hydrothermal ageing compared with zeolite-based HC-SCR catalysts. The metal in the HC-SCR catalysts can be present in the form of an oxide, but as the skilled person will appreciate, in use the oxide may react with exhaust gas

components to form a hydroxide, a carbonate, a sulfate or a nitrate, for example. All compound forms of the metal are embraced by the present invention.

5 The supported metal can be a transition metal such as V, Cu, Cr, Ni, Mn, Fe, Ga or Co or mixtures of any two or more thereof. Presently, copper is the preferred transition metal. Catalysts can become sulfated in use through contact with sulfur species in the exhaust gas derived from HC fuel or HC lubricant. Most preferably the catalysts are pre-sulfated, i.e. by sulfating the catalyst prior to inserting it into an exhaust system.

10 Without wishing to be bound by theory, we believe that supports capable of forming particularly stable sulfates are more useful in the present invention because they have increased acidity compared with the non-sulfated support. The support can comprise alumina, titania, zirconia, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof. In particular the alumina can be of any particular type, 15 such as α , θ , δ or γ . However, presently, the γ form is preferred. The support can be stabilised (or doped) with Si, W, Mo, Nb or P. Dopants are typically present in the form of oxides but in use may be in the form of sulfates, nitrates, hydroxides etc.

A preferred HC-SCR catalyst according to the invention is at least one of alumina 20 supported copper and zirconia supported copper. A mixture of CuO , Al_2O_3 and CuAl_2O_4 is particularly preferred.

The transition metal loading of the support material can be chosen as appropriate, but we have found that loadings of from between 5 and 20 wt.% based on the support are 25 adequate.

The preferred catalysts for use in the present invention are advantageous as they have lower selectivity to N_2O formation than Pt-based catalysts and generally are active at higher temperatures than Pt-based catalysts. Lean hydrothermal ageing and lean 30 hydrothermal sulfur ageing (LHSA) of Cu-zeolite catalysts at 550°C for prolonged periods of e.g. 16 hours or more leads to severe deactivation. However, we have found that LHSA of 10 wt.% $\text{Cu}/\text{Al}_2\text{O}_3$ and 10 wt.% Cu/sulfated zirconia actually improves HC-SCR activity.

We believe that the increase in activity obtained by the sulfur promotion, i.e. the sulfation of the catalyst, arises due to increased HC activation by acidic sulfur sites and formation of coke species that are active for HC-SCR. The activation step in which the catalyst is pre-treated with hydrocarbon leads to increased activity as it effectively leads to storage of activated hydrocarbon species on the catalyst.

One interesting application of the preferred catalysts according to the invention is that it may not be necessary to continuously inject additional HC into the exhaust system upstream of the HC-SCR catalyst in order to improve the efficiency of NO_x reduction over the HC-SCR catalyst (so-called "Active DeNO_x"). Injection of hydrocarbon at 200-300°C in diesel applications followed by a temperature ramp in a gas mix not containing HC still results in good NO_x conversion. This process can effectively improve fuel economy by allowing more efficient use of the hydrocarbon for NO_x reduction.

This observation has application in treating HC emissions at lower exhaust gas temperatures, e.g. immediately after cold-start, wherein the catalyst is formulated in a composition including an adsorber, such as a zeolite e.g. ZSM-5, β -zeolite or mordenite, as explained in our EP-B-830201. The adsorber can adsorb HC at relatively low temperatures, below the temperature at which the HC-SCR catalyst is active for reducing NO_x, and desorb the HC at a relatively higher temperature when the catalyst is active. By matching the temperature window of adsorption/desorption of the adsorber with the temperature window of activity of the catalyst it is possible to improve HC treatment in the exhaust system.

In a further aspect, the HC-SCR catalysts and catalyst compositions according to the invention can be used in the exhaust treatment system of an internal combustion engine, preferably a diesel engine and most preferably a heavy-duty diesel engine (as defined by the relevant European or US Federal or California State legislation). However, the engine can be powered by alternative fuel means such as CNG, LPG or methanol, and engines powered by these alternative fuels are within the scope of the present invention.

The preferred catalysts according to the invention can be made by methods known in the literature. For example, as described in G. Delahay *et al.*, Journal of

Catalysis 175 (1998) 7, the Figueras *et al.* paper above or J. Pasel *et al.* App. Cat. B: Environ. 25 (2000) 105. These include sulfation using sulfuric acid, impregnation using a sulfate-containing metal pre-cursor e.g. CuSO_4 (aq), or by lean hydrothermal sulfur ageing.

5

As the skilled person will be aware, hydrocarbon fuels such as diesel fuels include sulfur-containing species. As a result, the exhaust gases produced by its combustion can include sulfur-containing species such as SO_x , e.g. SO_2 and SO_3 , or organic species which can be adsorbed to volatile organic fraction or soluble organic fractions of the particulate matter. Thus, catalysts inserted in the exhaust system of an engine will be exposed to sulfur-containing species and may be sulfated as a result. Accordingly, one process for making the catalysts according to the present invention is to insert an unsulfated catalyst in the exhaust system of an engine and allowing it to become sulfated. However, pre-sulfation of the catalyst is presently preferred because control of the sulfation process can be controlled.

15

According to a further aspect, the invention provides a method of reducing NO_x with a hydrocarbon in an exhaust gas of an internal combustion engine using a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst including a metal on a support which support comprises alumina, titania, zirconia or, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, which process comprising intermittently coking the first catalyst at a catalyst temperature between that at which oxidation of hydrocarbon commences on the first catalyst and peak NO_x conversion occurs by contacting the first catalyst with a hydrocarbon and contacting the coked first catalyst with the exhaust gas at a temperature where NO_x reduction occurs, and converting NO_x in the exhaust gas over the second HC-SCR catalyst with hydrocarbon which slips the first HC-SCR catalyst.

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In order that an aspect of the invention may be more fully understood, reference will now be made to the following Examples by way of illustration only and with reference to the accompanying drawings, in which:

Figure 1 is a graph showing the adsorption of $n\text{-C}_{10}\text{H}_{22}$ (400 ppmC₃) in full gas mixture without NO_x at 250°C and 300°C on a sulfated 10%Cu/Al₂O₃ catalyst;

Figure 2 is a graph showing NO_x reaction with the pre-adsorbed $n\text{-C}_{10}\text{H}_{22}$ of
5 Figure 1;

Figure 3 is a graph showing the NO_x and CO conversions of a Cu/sulfated zirconia catalyst formed by CuSO₄ impregnation onto ZrO₂;

10 Figure 4 is a graph showing the NO_x and CO conversions of a Cu/ZrO₂ catalyst formed by Cu(NO₃)₂ impregnation onto ZrO₂;

Figure 5 is a graph showing the effect of pre-“coking” the catalyst of Figure 3 on NO_x and CO conversions;
15

Figure 6 is a graph showing the effect of pre-“coking” the catalyst of Figure 1 on NO_x conversions; and

Figure 7 is a graph comparing the NH₃ TPD for the catalyst of Figures 3 and 4
20 and a sulfated ZrO₂ control.

EXAMPLE 1

Cu/Al₂O₃ powder catalyst preparation

25

Catalyst preparation followed known methods in the literature, such as those described by Delahay, Figueras and Pasel mentioned above. More specifically, the 10wt%Cu/Al₂O₃ catalyst (based on the total weight of the support) was prepared by wet impregnation using a copper nitrate (aq) copper precursor. The catalyst was dried and
30 calcined in air at 500°C for 2 hours and then at 800°C for a further 2 hours. XRD analysis suggests that this process produces a product including a mixture of CuO, Al₂O₃ and CuAl₂O₄. Sulfation was by lean hydrothermal ageing in air, SO₂ (50 ppm) and 5% H₂O at 550°C.

EXAMPLE 2**HC-SCR NO_x activity of Cu/Al₂O₃ powder catalyst**

The activity of the powder copper catalysts of Example 1 were measured at a mass hourly swept volume (MHSV) of 200 litres per hour per gram (0.6 gram and 2 litres per minute) in a simulated exhaust gas mixture of 200ppm NO_x, 400ppmC₃ (propene equivalent [measured by FID/THC analyser]) n-C₁₀H₂₂, 14% O₂, 5.1% CO₂, 750ppm CO and 20ppm SO₂. The gas mixture was adjusted to remove at least one of the HC and NO_x as appropriate.

Figure 1 shows HC consumption over the catalyst at 250°C or 300°C in the absence of NO_x. The HC was then removed from the gas mixture and the catalyst was allowed to cool to 200°C. NO_x was then added to the gas mixture and the temperature was ramped up at 10°C per minute to 550°C. As a control, an identical sample was also exposed at 250°C without NO_x or HC present. In another test, after HC exposure at 250°C, the sample was ramped up in NO₂. The NO_x conversion using the pre-adsorbed HC is shown in Figure 2.

As can be seen, in the absence of any adsorbed HC, the NO_x conversion was negligible, whilst pre-adsorbing the HC gives significant NO_x conversion with the highest conversion activity achieved with the NO₂.

EXAMPLE 3**Preparation of Cu/ZrO₂ and Cu/Al₂O₃ pelletised powder catalyst**

A sulfated 10wt%Cu/ZrO₂ was prepared following known methods in the literature by impregnation of ZrO₂ with CuSO₄, drying and calcining the powder in air at 500°C. This support is referred to as "SZ" or sulfated zirconia. For comparison, a non-sulfated 10wt%Cu/ZrO₂ catalyst was prepared by impregnating of ZrO₂ with Cu(NO₃)₂ (aq) and calcining in the same way. A 10wt%Cu/Al₂O₃ powder catalyst was prepared similarly to Example 1, except that no 800°C calcination step was performed and the sulfation was done with sulfuric acid. The powder catalysts were pelletised and particle sizes in the range of 250<d<355 µm were used for subsequent experimentation.

EXAMPLE 4**HC-SCR NO_x activity of Cu/ZrO₂ pelletised powder catalyst**

The activity measurements have been performed with n-C₁₀H₂₂ or propene as the HC species. The following conditions were used: NO 200ppm, CO 745ppm, CO₂ 5.1%, O₂ 14%, H₂O 4.6%, 400ppmC₃ (propene equivalent [measured by FID/THC analyser]), SO₂ 20ppm, N₂ balance at a MHSV of 200 L h⁻¹ g⁻¹. Unless otherwise indicated the data were collected in ramp up mode, 10°C/min, from 150°C.

Figure 3 shows the NO_x and CO conversions of the Cu/SZ catalyst of Example 3. With repeat runs the NO_x conversion and CO production both increased. Figure 4 shows the Cu/ZrO₂ system made with a nitrate precursor of Example 4. The NO_x conversion is lower, though still increases slightly with repeat ramps, and there is no sign of CO production.

Conclusions

Since we have shown previously that a sulfated Cu/ZrO₂ catalyst prepared by impregnation of Cu(NO₃)₂ on sulfated ZrO₂ are strongly inhibited by water (see G.P. Ansell paper above), these results suggest a competition between water and a hydrocarbon-derived component for active sites on the catalyst. The formation of this hydrocarbon-derived component would appear to be promoted by the increased acidic nature of the catalyst.

Peak NO_x conversion appears to be related to the ability of the catalyst to produce CO indicating that the hydrocarbon is being only partially oxidised in the temperature window for NO_x conversion. We have also observed that the NO_x conversion of these materials increases with repeated use.

EXAMPLE 5

In order to show that the improvement in NO_x conversion with repeat use of the systems described in Example 4 is linked to the formation of coke species on the catalyst

surface, we performed tests to probe the effect of catalyst pre-treatment on subsequent NO_x conversion activity. In these tests the catalyst is held at constant temperature for a period of time in the gas mix described in Example 4, then quickly cooled it to 150°C before increasing the temperature ramp-wise at 10°C/min.

5

Figure 5 shows the effect of this 'coking' procedure on the 10wt%Cu/SZ. Both CO production and NO_x conversion increase with the length of time the catalyst is "pre-treated" by exposing it to the full gas mix at 250°C. An explanation for this effect is that the pre-treatment effectively leads to storage of activated hydrocarbon species on the catalyst surface which are subsequently used for NO_x reduction. At the pre-treatment temperature, ~15% of the hydrocarbon is converted. In all these experiments the temperature ramp is started at 150°C at which temperature there is no hydrocarbon conversion and no effect of pre-treatment. This should avoid coking occurring before the temperature ramp begins. Figure 6 shows similar data for the pelletised sulfated Cu/Al₂O₃ catalyst according to Example 3. The CO production again increases with NO_x conversion for this catalyst.

EXAMPLE 6

In order to investigate the mechanism for improved NO_x conversion over a coked catalyst for use in the present invention, we tested a H₂SO₄ impregnated ZrO₂ catalyst using the synthetic gas mixture described in Example 4, also including 200ppm NO₂. Even after coking at 250°C this sample gave NO_x conversions significantly less than 10%. We believe, therefore, that the NO_x conversion mechanism for sulfated Cu/support catalysts may require some synergy between the Cu and the support. Figure 7 shows the NH₃ temperature-programmed desorption (TPD) profiles for the Cu/SZ (CuSO₄ precursor) and Cu/ZrO₂ (Cu(NO₃)₂ precursor) of Example 3 and a sulfated ZrO₂ control. The profile shows that the Cu/ZrO₂ (Cu(NO₃)₂ precursor) has similar acidity to the sulfated ZrO₂ sample but the NO_x conversion over the Cu-containing catalyst is higher.

The Cu/SZ (CuSO₄ precursor) sample has much higher acidity.

CLAIMS:

1. An exhaust system for an internal combustion engine, which exhaust system including a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst comprising
5 a metal on a support, which support comprises alumina, titania, zirconia or, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof, and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, wherein the exhaust system comprises means for coking the catalyst during normal engine operation.
- 10 2. An exhaust system according to claim 1, wherein the coking means includes means for introducing a hydrocarbon into an exhaust gas.
3. An exhaust system according to claim 2, wherein the hydrocarbon introducing
15 means comprises at least one of: means for injecting the hydrocarbon into the exhaust gas; means for adjusting the ignition timing of at least one engine cylinder; and means for adjusting the engine air-to-fuel ratio.
4. An exhaust system according to any preceding claim, wherein the hydrocarbon is
20 the fuel that powers the engine.
5. An exhaust system according to any preceding claim, wherein the coking means further comprises means for controlling the coking process, preferably in order that coking is intermittent.
- 25 6. An exhaust system according to claim 5, wherein the control means cokes the catalyst between temperatures at which hydrocarbon oxidation commences over the catalyst and peak NO_x conversion occurs.
- 30 7. An exhaust system according to claim 6, wherein the control means cokes the catalyst at between 200-450°C, preferably 250-350°C.
8. An exhaust system according to claim 5, 6 or 7, wherein the control means includes a pre-programmed electronic control unit.

9. An exhaust system according to any preceding claim, wherein the first HC-SCR catalyst supported metal is a transition metal.
- 5 10. An exhaust system according to claim 9, wherein the transition metal is V, Cu, Cr, Ni, Mn, Fe, Ga or Co or mixtures of any two or more thereof.
11. An exhaust system according to any preceding claim, wherein the first HC-SCR metal catalyst component is a metal oxide.
- 10 12. An exhaust system according to any preceding claim, wherein the support for the first HC-SCR catalyst is stabilised with Si, W, Mo, Nb or P.
13. An exhaust system according to claim 12, the first HC-SCR catalyst comprises
15 alumina supported copper or zirconia supported copper.
14. An exhaust system according to claim 13, wherein the first HC-SCR catalyst comprises a mixture of CuO, Al₂O₃ and CuAl₂O₄.
- 20 15. An exhaust system according to any preceding claim, wherein the metal loading in the catalyst is 5-20 wt.% based on the support.
16. An exhaust system according to any preceding claim, wherein the first HC-SCR catalyst is sulfated.
- 25 17. An exhaust system according to any preceding claim, wherein the second platinum-based HC-SCR catalyst is Pt/Al₂O₃.
18. An exhaust system according to any preceding claim, further comprising a HC
30 adsorber, preferably upstream of the supported metal catalyst according to claim 1.
19. An exhaust system according to claim 18, wherein the HC adsorber comprises a zeolite.

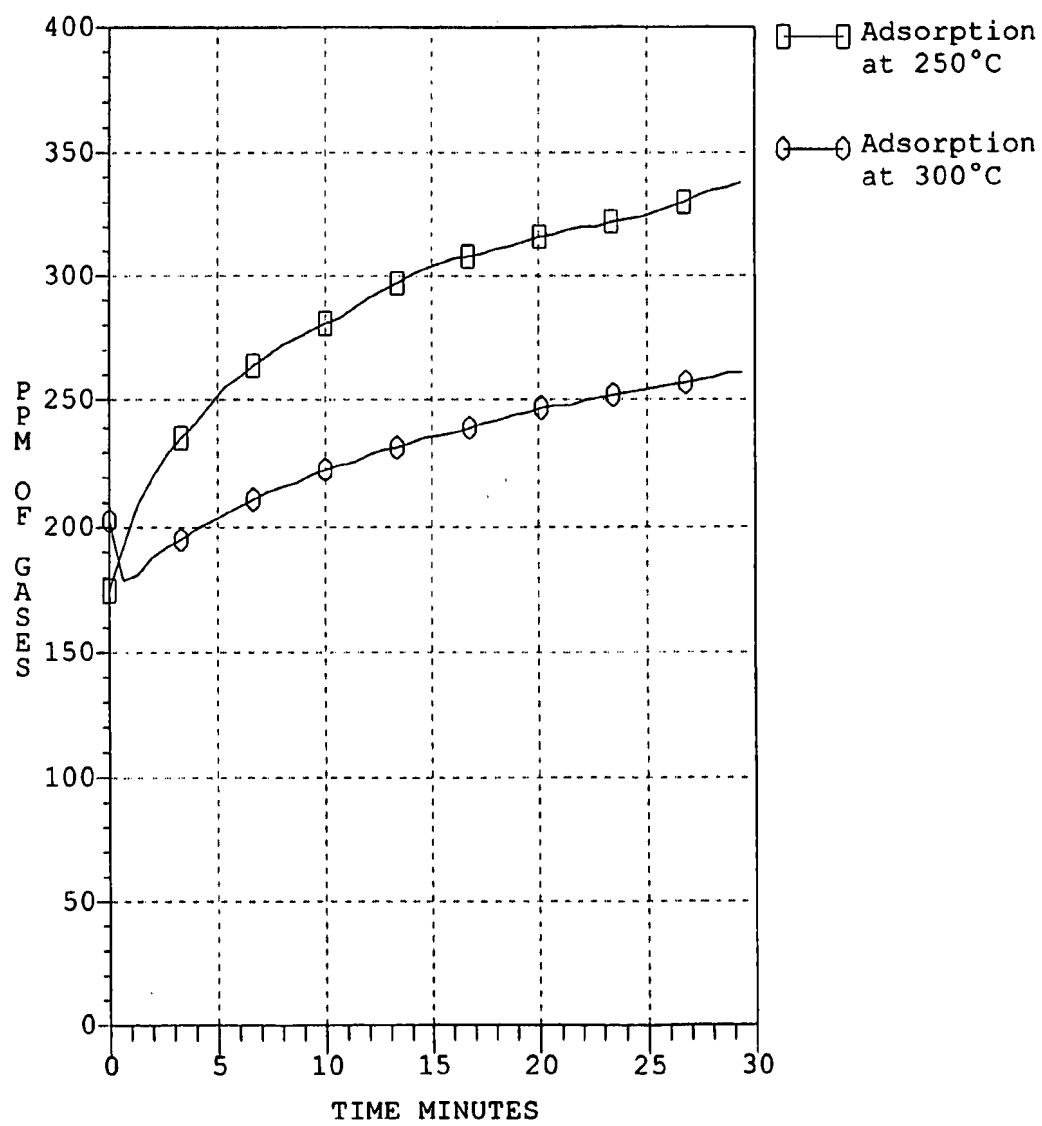
20. An internal combustion engine including an exhaust treatment system according to any preceding claim.

21. An engine according to claim 20, wherein it is a diesel engine, preferably a heavy-duty diesel engine.

22. A method of reducing NO_x with a hydrocarbon in an exhaust gas of an internal combustion engine using a first hydrocarbon selective catalytic reduction (HC-SCR) catalyst including a metal on a support which support comprises alumina, titania, zirconia or, non-zeolite silica-alumina or a mixture or mixed oxide of any two or more thereof and a second, platinum-based HC-SCR catalyst disposed with and/or downstream of the first HC-SCR catalyst, which process comprising intermittently coking the first catalyst at a catalyst temperature between that at which oxidation of hydrocarbon commences on the first catalyst and peak NO_x conversion occurs by contacting the first catalyst with a hydrocarbon and contacting the coked first catalyst with the exhaust gas at a temperature where NO_x reduction occurs, and converting NO_x in the exhaust gas over the second HC-SCR catalyst with hydrocarbon which slips the first HC-SCR catalyst.

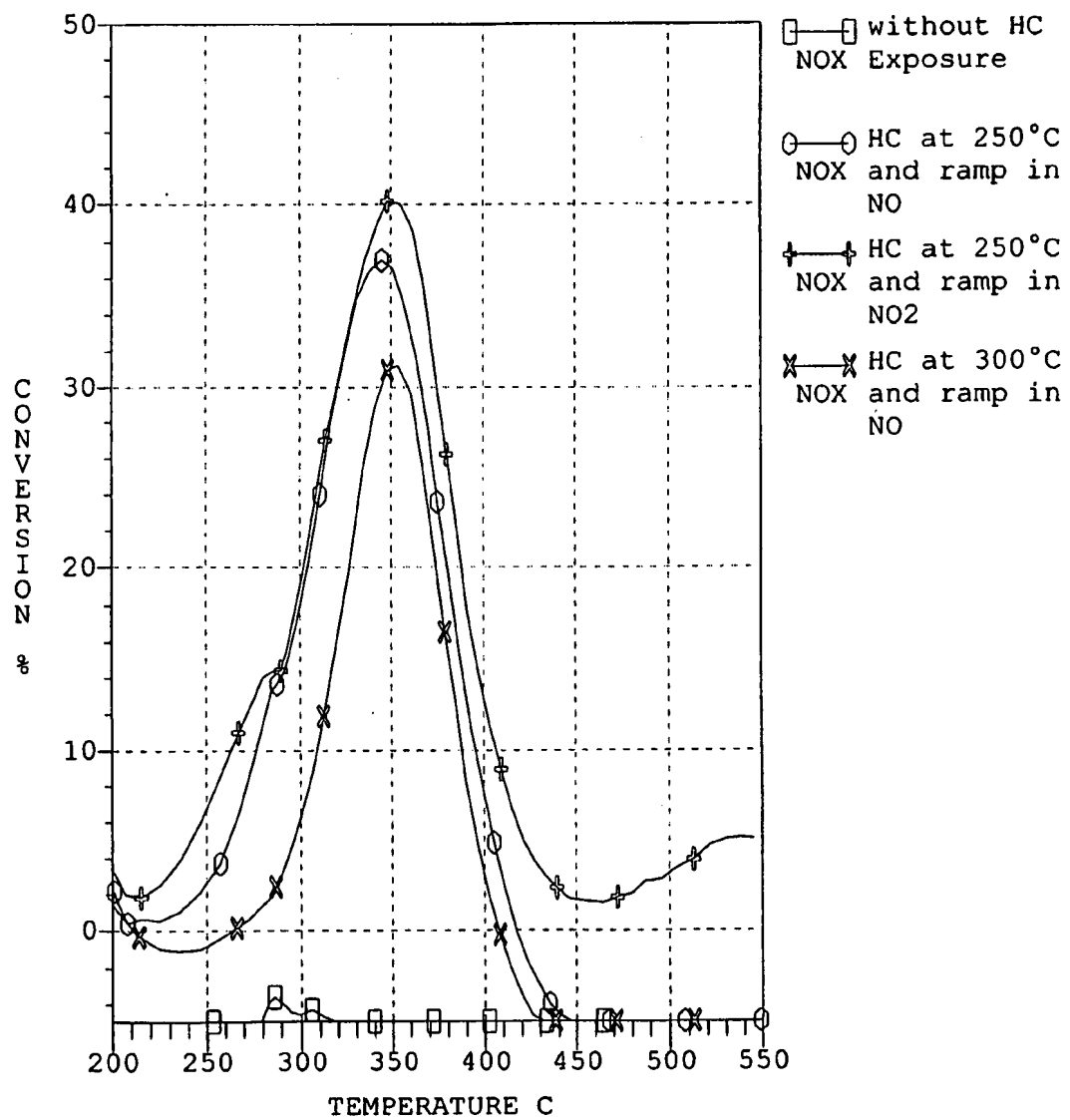
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Figure 1



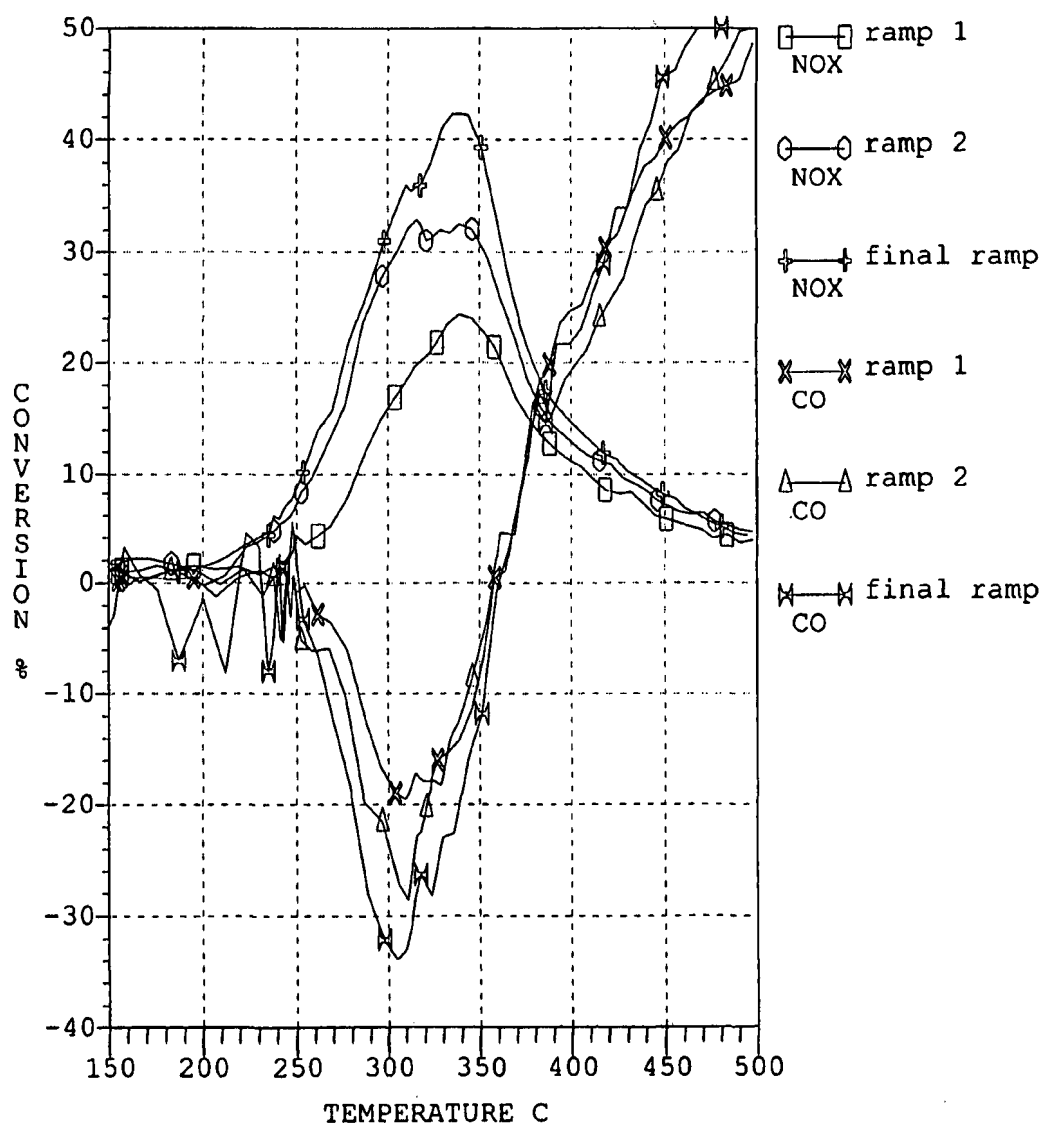
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Figure 2



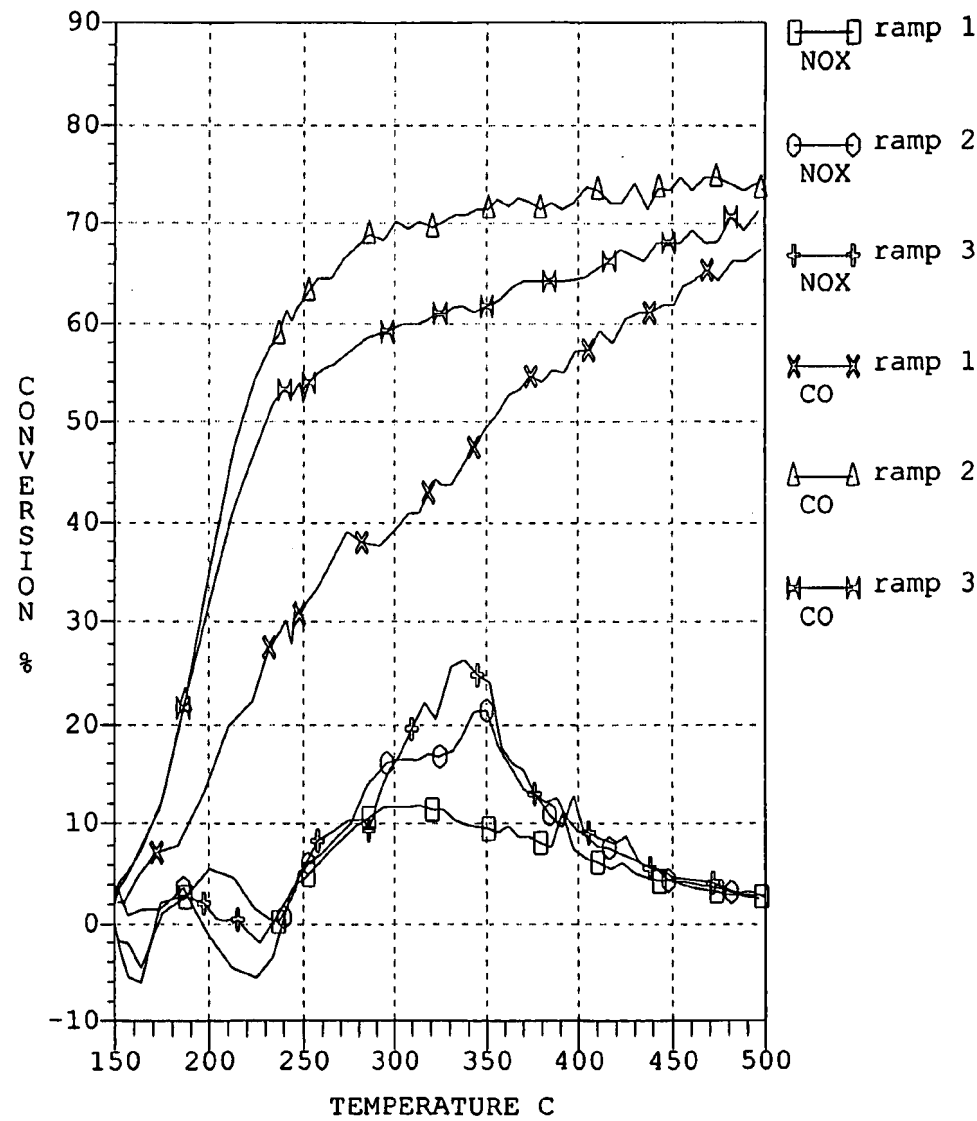
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Figure 3



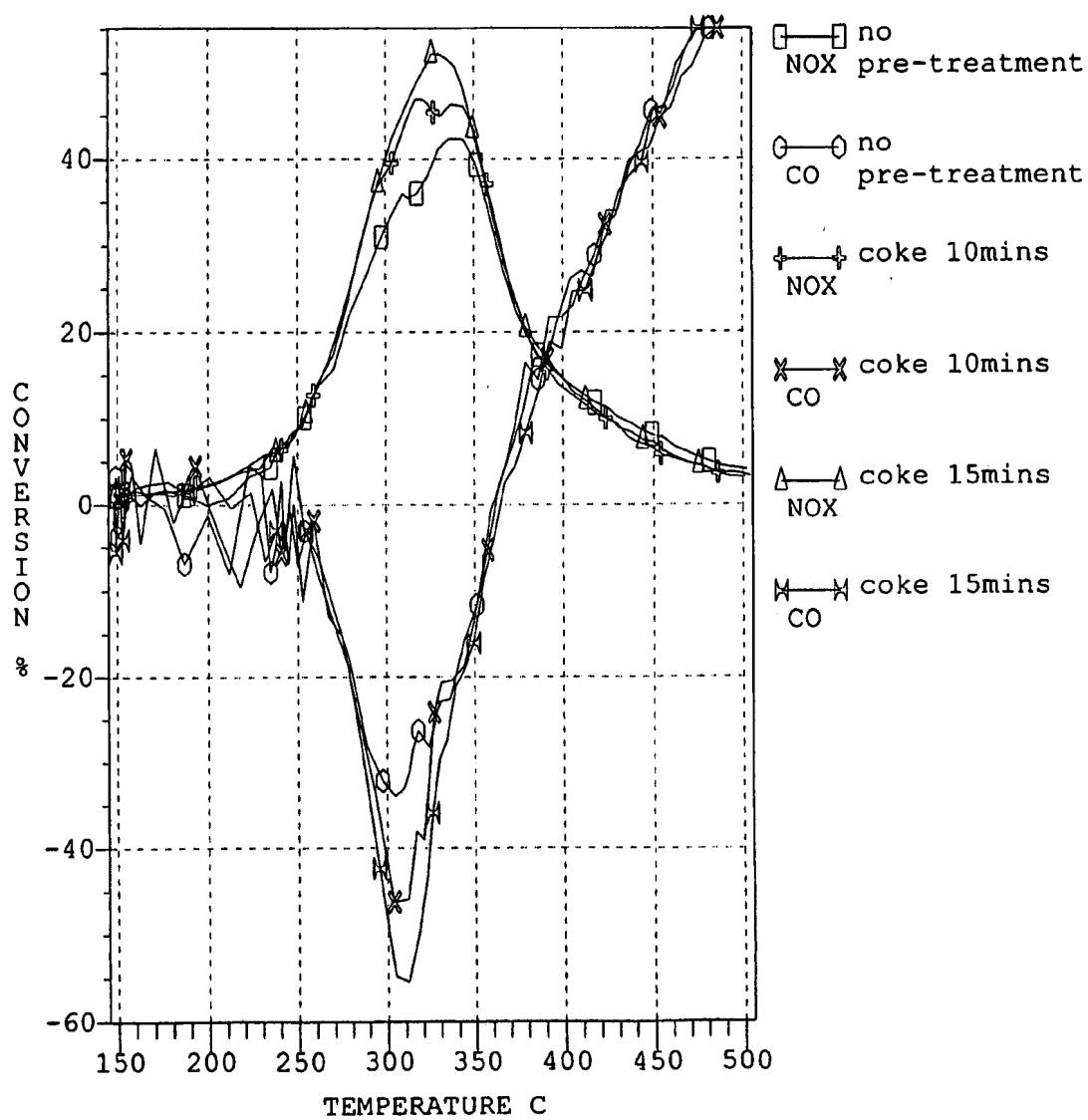
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Figure 4



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Figure 5



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Figure 6

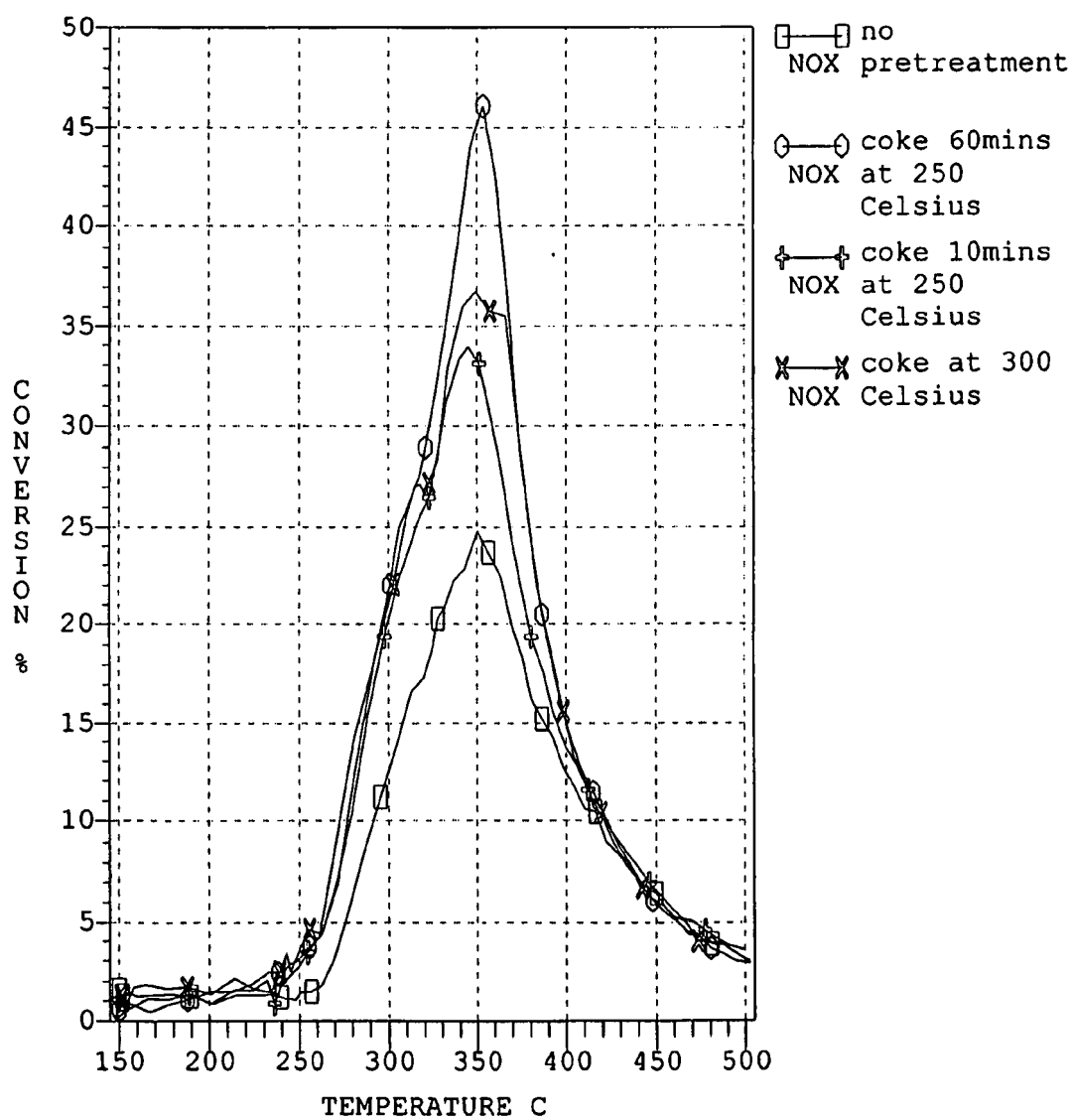
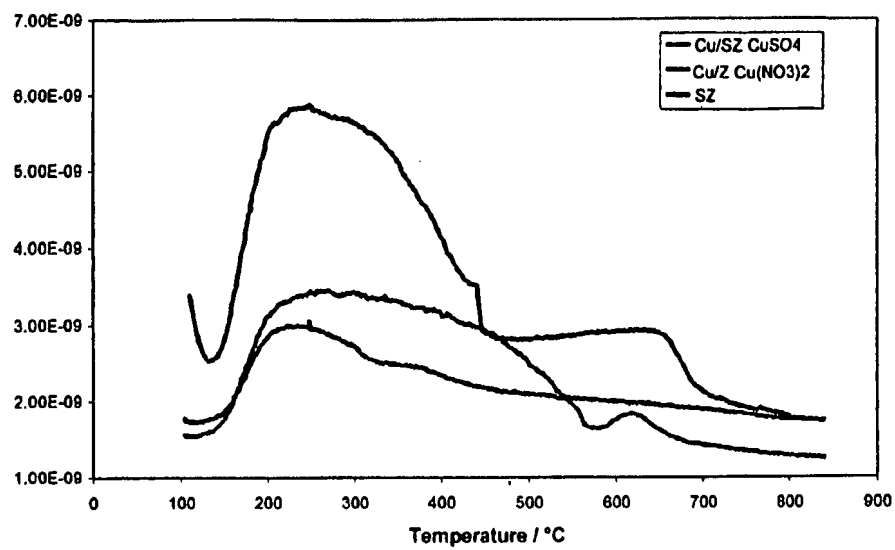


Figure 7

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 02/04606

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 947 235 A (MAZDA MOTOR) 6 October 1999 (1999-10-06) column 2, line 12 -column 3, line 9 column 12, paragraph 50 column 14, paragraph 57 column 16, line 1 - line 7 column 19, line 46 - line 55; claims 1-15; figure 1 ---	1-4, 9-15,17, 20-22
X	GB 1 458 514 A (TOYODA CHUO KENKYUSHO KK) 15 December 1976 (1976-12-15) page 2, line 56 -page 3, line 94 --- -/--	1-4, 9-15, 20-22

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Eijkenboom, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/04606

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